

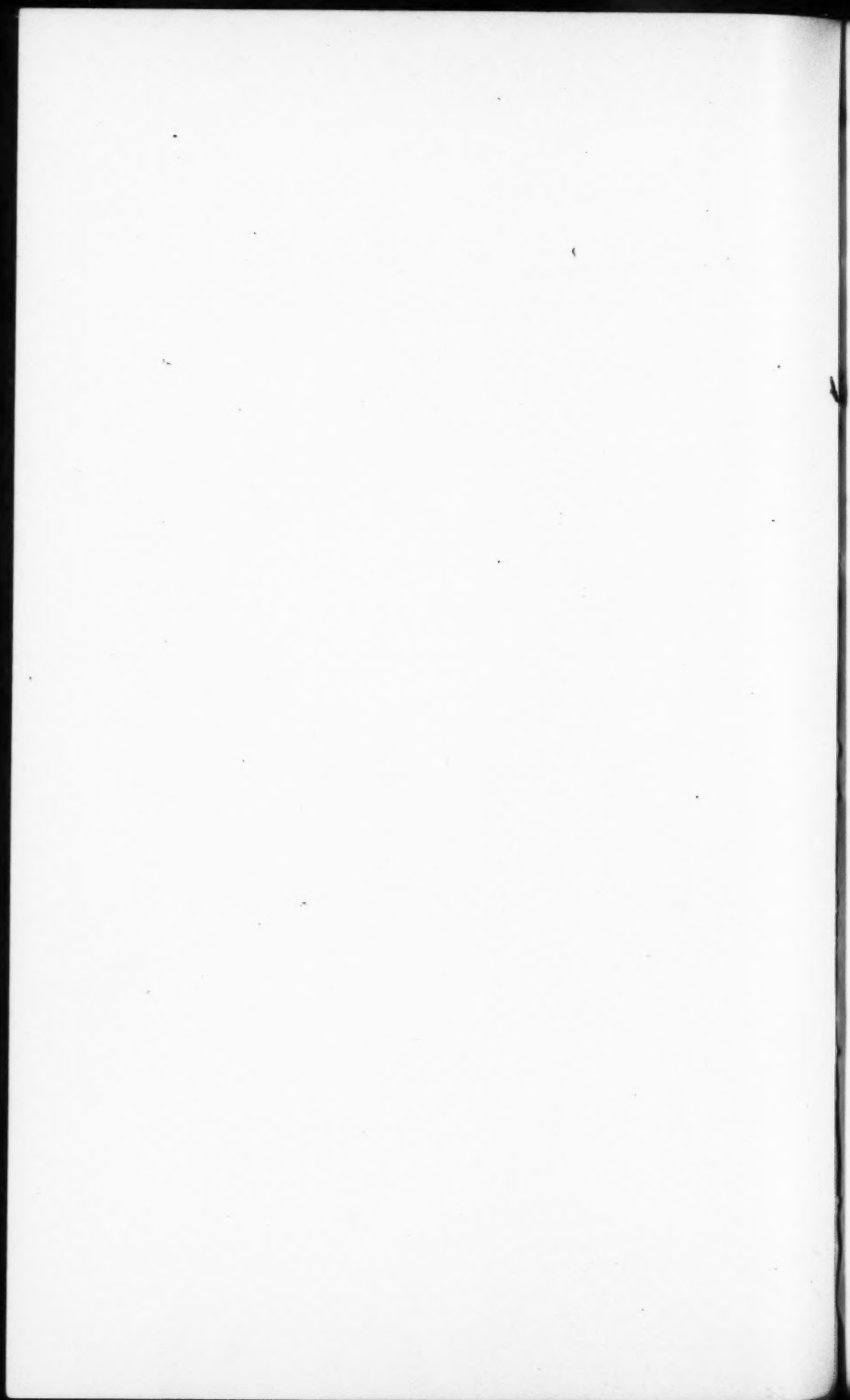
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THE ELECTRICAL RESISTANCE OF ALLOYS UNDER  
PRESSURE.

By C. W. UFFORD.



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## INTRODUCTION.

IN this paper, are presented measurements of the effect of hydrostatic pressures from atmospheric to 12000 kg/cm<sup>2</sup> on the electrical resistance of three series of alloys: lithium tin, bismuth tin, calcium lead; and one alloy of calcium and magnesium with 10 A% Mg. These three series were chosen since each consists of one metal whose resistance increases with pressure: lithium, bismuth and calcium; and another whose resistance decreases with pressure; tin and lead. In this way, a large variation of the pressure coefficient of electrical resistance as a function of the composition of the alloys is obtained. The pressure coefficients were measured at two temperatures for each series of alloys.

There are seven metals which increase in resistance as the pressure increases, the normal effect being for the resistance to decrease as the pressure increases: lithium, calcium, strontium, antimony, cesium, barium, cerium and bismuth. By including the most easily manipulated of these in the alloys, it is hoped to give a basis for explaining this abnormal effect which must be accounted for by a complete theory of electric conduction in metals.

## PREVIOUS EXPERIMENTS.

Bridgman<sup>1</sup> has measured the effect of pressures up to 12000 kg/cm<sup>2</sup> on the electrical resistance of a large number of elements and five commercial alloys, including the five elements bismuth, calcium, lead, lithium and tin used in preparing the alloys for these experiments. Bridgman's results are used here for the end points at zero

and one hundred per cent in the curves plotted with concentrations as abscissae.

Lisell<sup>2</sup> and Beckman<sup>3</sup> have measured the pressure coefficients of the binary alloys gold-silver, cadmium lead, gold-nickel, and copper-manganese up to pressures of 2700 atmospheres. There have been no measurements as far as we know on the series of alloys of these experiments.

#### EXPERIMENTAL METHOD.

The composition of the alloys was determined by weighing the two metals before they were alloyed. It was necessary to weigh lithium and calcium under white petroleum oil to prevent their being oxidized. The metal, covered with an oil film, was dipped into petroleum ether. Just as this evaporated, the metal was dropped dry into the weighed crucible of oil. The oxidation of lithium after this process was slight, and that of calcium even less. The alloys weighed from one to five grams.

The alloys were made by melting the two metals together in vacuum in an electric furnace. Bismuth and tin were melted in a pyrex tube connected directly to the vacuum pump. Lithium and tin were put in a small steel tube inserted in a steel cylinder, into the top of which a plug was screwed. The interior of the plugged steel cylinder was connected with the vacuum outside by a hole drilled along the axis of the plug, starting from the inside, not extending straight through the plug, but intersecting in an acute angle a hole drilled in from the outside of the plug. This largely prevented the lithium vapor from escaping from the bomb by forcing it to turn an acute angle away from the pump in its effort to get out. The metals in this steel bomb, placed in a continuously evacuated quartz tube, were melted in an electric furnace.

Calcium and lead reacted so violently that another method was used to prepare them. The metals were compressed mechanically into a small Chromel "A" cylinder fitted with a plug, through which a small hole was drilled. This cylinder was then sealed into an evacuated quartz tube, together with a steel cap containing a small amount of metallic calcium. This tube, separate from the vacuum pump, was heated in an electric furnace. As calcium sublimed, the vapor pressure due to the calcium in the cap was equal to that inside the cylinder containing the alloy, provided that the entire quartz tube was at a uniform temperature, so that there was no tendency for the calcium to escape from the cylinder. In spite of this, the



reaction of the calcium with lead was so violent that the alloy flowed freely from the containing cylinder.

Some calcium-lead alloys rich in calcium were made in an atmosphere of argon gas under a pressure of four atmospheres to prevent the alloy from escaping from the cylinder, but the argon had practically no effect. Finally, the metals were put in a cylinder with a metal plug screwed tightly in against them, without any hole in the plug, so that it was impossible for any of the alloy to escape. This was the most successful way of making lithium-tin alloys from 0 to 30 A% tin, and calcium-lead alloys from 50 to 100 A% calcium. No lithium-tin alloys from 10 to 30 A% tin, nor calcium-lead alloys from 50 to 80 A% calcium were measured, because, even when it was possible to make them by this final method, it was so difficult to extrude them into wires suitable for mounting in the pressure apparatus, and the wires obtained were so brittle that all attempts failed. After melting, the cylinder containing the alloy was turned off in a lathe, a considerable portion of the alloy being cut away in order to remove any contamination from the cylinder.

The alloys were made into wires by extruding them in a cylindrical die made from Bessemer steel by cutting a one-quarter-inch hole to hold the alloy, enlarging the top of this hole to half an inch, and drilling through the bottom of it a hole .052 inch in diameter, which determined the diameter of the wire. The die was set in an arbor press with the lower part of the die immersed in a test tube of white petroleum oil to prevent the alloy's being oxidized as it came out hot.

The pressure was exerted by a piston one-quarter of an inch in diameter at the bottom, one-half an inch at the top, corresponding with the hole in the die. The upper part of the piston was made larger than the lower to give strength to the threads holding a cross bar by which it was removed from the die. This also prevented the piston from bending under pressure.

After the alloy to be extruded was put in the die, copper and steel washers were driven down hard on top of it. A plug, made to fit the reamed hole in the bottom of the die, prevented the hole from becoming clogged with alloy oxidized when the die and alloy were heated in an electric furnace to the proper temperature for extruding. The alloys rich in lithium and calcium were so brittle that they had to be heated nearly to the melting point before they could be extruded. The most satisfactory extrusion temperature was found to be about eight-ninths of the melting temperature of the alloy.

The extruded wire was set in a pyrex test tube, mounted on top of the three-terminal plug which screwed into the lower cylinder of the pressure apparatus. The method of measuring the resistance of the alloy and its change with pressure on a potentiometer has been described by Bridgman.<sup>1b</sup>

#### ACCURACY OF THE RESULTS.

From the calibration of the manganin pressure gauge against a standard gauge,<sup>4</sup> the probable error in the pressure reading is shown to be less than .1%. The errors in measuring the resistance arose from reading the slide wire, thermoelectromotive forces, poor contacts, chemical action, change of state of the alloy, hysteresis, and lack of temperature control. These disturbances tend to prevent the points taken with increasing and decreasing pressure from lying on a smooth curve. Therefore, in order to estimate the probable error in the change of resistance produced by the pressure apparatus for all these different reasons, the curve in which the points were most widely scattered was chosen to calculate the average deviation of all the points from a smooth curve. This gave a probable error of .4%. It therefore may be assumed that the pressure coefficients of resistance of the actual specimens measured are correct to within .5%.

The accuracy of the temperature coefficients is not as great as that of the pressure coefficients, since the former were calculated from the measurements taken at atmospheric pressure in measuring the change of resistance with pressure at two different temperatures. The two measurements were often taken on different days, and represent a single observation and not an average value. The average temperature coefficients from 0 to 30°C of the alloys of the bismuth-tin series at 20.31 and 30.20 A% tin were found by extrapolating the average coefficients from 30 to 75° and 30 to 50°C respectively, since no measurements were made on these alloys at 0°C.

The greatest error is in the composition of the alloys themselves, especially those rich in lithium and calcium. The weight could be found to within .2 mg. on the analytical balance used, which gave a probable error in the composition of the alloys of the bismuth-tin series of  $\pm .02\%$ . The bismuth used in the alloys was Kahlbaum's grade "K," the following analysis for which is given by Bucher.<sup>5</sup> In 100 grams of bismuth:

silver,	scarcely a trace
lead,	trace
copper,	1.0 mg.      and
iron,	.1 mg.

A sample of tin from the Bureau of Standards was used in both the bismuth-tin and lithium-tin series. The lithium was Kahlbaum's grade "K." The calcium was from a sample purified specially for Professor Bridgman in the Cornell University Chemical Laboratory. The lead was the Bureau of Standards melting-point lead, for which Bridgman<sup>6</sup> gives the following analysis:

Ag	.0002 to .0003%
Sb	.0019 to .0028%
Sn	.0008 to .0011%
Cu	.0003 to .0004%
Fe	.0004 to .0006%
As, Bi, Zn, Co, Ni	trace
Cd Mn	none
Lead (by difference)	99.9948+%

In the two lithium-tin alloys with 9 and 10 A% tin, 2 or 3 A% excess lithium was melted with the alloy to allow for vaporization. The vaporization and violence of the reaction was such in the alloys rich in lithium and calcium as to make their composition doubtful, so that the alloy with 55.7 A% lead, which vaporized and flowed most violently, was analyzed chemically, giving an error of 5.7 A% in its composition. This is a fair estimate of the error in composition of the alloys rich in lithium and calcium.

#### RESULTS.

The results are presented in the form of tables. The average pressure coefficient of resistance to 12000 kg/cm<sup>2</sup> ( $1/R_0$ ) ( $\Delta R/\Delta p$ ) and the average temperature coefficient between the two temperatures at which measurements were made for each series are given in Table I. The average pressure coefficient to 12000 kg/cm<sup>2</sup> is the slope of the straight line drawn from the origin to the point corresponding to 12000 kg/cm<sup>2</sup> on the curve of relative change of resistance with pressure. In order to reproduce this curve, the deviation of the points from this straight line at 2, 4, 6, 8 and  $10 \times 10^3$  kg/cm<sup>2</sup> are given in Table II. The deviation at atmospheric pressure and at 12000 kg/cm<sup>2</sup> is then zero. Thus, in order to find the relative change of resistance at any pressure and the temperature of one of the sets of measurements, the average pressure coefficient to 12000 kg/cm<sup>2</sup> is multiplied by the given pressure, as found from the deviation curve drawn through the points given in Table II. The deviation curves are in general approximately parabolas.

As an example, find the relative change of resistance of an alloy of bismuth and tin with 10.01 A% tin at 0°C and 8000 kg/cm<sup>2</sup>. From Table I the average pressure coefficient of a bismuth-tin alloy of 10.01 A% tin at 0°C is  $-.041135$ . The relative linear change of resistance is thus  $-.041135 \times 8000 = -.09080$ . From Table II, the deviation from linearity for a bismuth-tin alloy of 10.01 A% tin at 0°C is found to be  $-.00313$ . The sum of these two is  $-.09393$ , which is the relative decrease in resistance due to a pressure of 8,000 kg/cm<sup>2</sup>.

The curves showing the relative change of resistance under pressure of the bismuth-tin alloy of .53 A% tin were too widely separated for increasing and decreasing pressure to plot a curve of deviation from a straight line. This separation is probably due to a change of state of the alloy. This is the one alloy measured which showed a change of sign of the pressure coefficient during the measurements, since the resistance first increases to a maximum and then falls as the pressure increases. The relative change of resistance is given for the pressures up to 12000 kg/cm<sup>2</sup> in Table III. The pressure coefficient and deviations from linearity of the relative change of resistance for the single calcium-magnesium alloy, with 10 A% mg., are included in Tables I and II.

TABLE I.

PRESSURE AND TEMPERATURE COEFFICIENTS OF ELECTRICAL RESISTANCE.  
LITHIUM-TIN SERIES.

Composition A% Sn	Average coefficient 0-12000 Kg/cm <sup>2</sup>		Temperature coefficient 30-75° C
	30° C	75° C	
0	.0,772	.0,772	.00398
9.0	.0,9047	.0,9374	.00989
10.0	.0,8634	.0,9046	.00284
30.1	— .0,1062	— .0,1063	.00385
40.0	— .0,6595	— .0,6864	.00271
71.4	— .0,8419	— .0,8381	.00173
95.1	— .0,8886	— .0,9017	.00415
100.0	— .0,9295	— .0,9434	.00394

## CALCIUM-LEAD SERIES.

A% Pb			
0	.0,1236	.0,1172	.00304
9.5	.0,1434	.0,1502	.00390

TABLE I.—Continued.

## CALCIUM-LEAD SERIES.

Composition A% Pb	Average coefficient 0-12000 Kg/cm <sup>2</sup>		Temperature coefficient 30-75°C
	30°C	75°C	
17.5	.041382	.041516	.00312
18.8	.041422	.041374	.00294
29.6	— .03931	— .054127	.00474
55.7	— .04524	— .054894	.00260
63.8	— .057478	— .057424	.00278
74.8	— .041065	— .059997	.00303
90.0	— .041131	— .041144	.00333
100.0	— .041224	— .041243	.00375

## PRESSURE AND TEMPERATURE COEFFICIENTS OF ELECTRICAL RESISTANCE.

## BISMUTH-TIN SERIES.

Composition A% Sn	Average coefficient 0-12000 Kg/cm <sup>2</sup>		Temperature coefficient 0-30°C
	30°C	0°C	
0	.042129	.04223	.00392
Kahlbaum	.042498	.04269	.0028
.13	.042331	.042220	— .000976
.53	.047205	— .04910	— .0444
.89	— .044178	— .048998	.0475
5.02	— .041034	— .041166	.00270
10.01	— .041053	— .041135	.00323
20.32	— .049729		.00409
30.20	— .049451		.00332
39.87	— .049216	— .049126	.00355
50.39	— .048998	— .048856	.00350
68.51	— .048185	— .047946	.00367
90.00	— .047621	— .047403	.00375
97.99	— .048131	— .048008	.00455
100.00	— .049295	— .049204	.00433

## CALCIUM-MAGNESIUM SERIES.

A%Mg	0°C	30°C	
	Average 0-6000 Kg/cm <sup>2</sup>		
10.0	.041636	.041496	.00226

TABLE II.  
DEVIATIONS FROM LINEARITY.

LITHIUM-TIN SERIES. (30°C)		Pressures				
Composition A% Sn		2000	4000	6000	8000	10000
0						
9.0	—	.0396	— .00170	— .00267	— .00276	— .00202
10.0	—	.00385	— .00524	— .00436	— .00331	— .00220
30.1	—	.00916	— .0122	— .01189	— .00874	— .00458
40.4	—	.00275	— .00368	— .00389	— .00338	— .00168
71.4	—	.00851	— .00900	— .00741	— .00524	— .00288
95.12	—	.00236	— .00378	— .00410	— .00380	— .00204

LITHIUM-TIN SERIES.  
(75°C)

0						
9.0		No Deviation				
10.0	—	.00197	— .00377	— .00451	— .00426	— .00286
30.1	—	.00860	— .01152	— .01045	— .00796	— .00497
40.4	—	.03993	— .00201	— .00288	— .00287	— .00199
71.4	—	.00419	— .00753	— .00900	— .00802	— .00505
95.12	—	.00215	— .00341	— .00391	— .00358	— .00223

CALCIUM-MAGNESIUM SERIES.  
(0°C)

A% Mg					
10.0	— .00306	— .00516	— .00590	— .00519	— .00324

CALCIUM-MAGNESIUM SERIES.  
(30°C)

10.0		No Deviation				
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BISMUTH-TIN SERIES.  
(0°C)

Composition		Pressures				
A% Sn	2000	4000	6000	8000	10000	
.13	.0133	.01969	.0211	.02014	.0170	
.530	Deviation not calculated					
.89	.00236	.00358	.00331	.00226	.00121	
5.02	— .00130	— .00200	— .00230	— .00186	— .00108	
10.01	— .00201	— .00299	— .00343	— .00313	— .00243	
20.32						
30.20						

TABLE II.—(Continued).

## BISMUTH-TIN SERIES.

(0°C)

Composition A% Sn	Pressures				
	2000	4000	6000	8000	10000
39.87	— .00264	— .00384	— .00418	— .00375	— .00260
50.39	— .00211	— .00335	— .00390	— .00340	— .00206
68.51	— .00180	— .00336	— .00373	— .00319	— .00188
90.00	— .00902	— .00141	— .00161	— .00156	— .00120
97.99	— .00221	— .00296	— .00321	— .00280	— .00188

## BISMUTH-TIN SERIES.

(30°C)

.13	.00346	.00616	.00812	.01012	.00947
.530	.01433	.02524	.02764	.02205	.0140
.89	.00926	.01321	.01348	.01151	.00667
5.02	.00183	.00496	.00522	.00417	.00248
10.01	— .00654	— .00107	— .00121	— .00119	— .00934
20.32	— .00379	— .00136	— .00170	— .00144	— .00705
30.20	— .00160	— .00258	— .00284	— .00241	— .00144
39.87	— .00197	— .00311	— .00342	— .00316	— .00197
50.39	— .00171	— .00309	— .00354	— .00334	— .00232
68.51	— .00213	— .00342	— .00376	— .00338	— .00194
90.00	— .00160	— .00274	— .00301	— .00262	— .00157
97.99	— .00224	— .00296	— .00321	— .00281	— .00185

## CALCIUM-LEAD SERIES.

(30°C)

A% Pb					
9.52	— .00510	— .00880	— .00915	— .00769	— .00507
17.49	— .00405	— .00740	— .00830	— .00688	— .00463
18.80	— .00377	— .00659	— .00730	— .00615	— .00403
29.61	— .00141	— .00236	— .00259	— .00236	— .00159
55.7	— .00235	— .00317	— .00343	— .00300	— .00196
63.78	— .00229	— .00360	— .00386	— .00346	— .00230
74.76	— .00427	— .00620	— .00660	— .00480	— .00368
90.00	— .00353	— .00591	— .00631	— .00541	— .00339

## CALCIUM-LEAD SERIES.

(75°C)

9.52	— .00420	— .00756	— .00824	— .00672	— .00409
17.49	— .00403	— .00690	— .00785	— .00698	— .00461
18.80	— .00385	— .00696	— .00788	— .00636	— .00397
29.61	— .00147	— .00300	— .00322	— .00297	— .00202

TABLE II.—(Continued).

CALCIUM-LEAD SERIES.  
(75°C)

<i>Composition</i> A% Pb	<i>Pressures</i>				
	2000	4000	6000	8000	10000
55.7	— .00197	— .00329	— .00339	— .00285	— .00178
63.78	— .00182	— .00308	— .00360	— .00314	— .00200
74.76	— .00343	— .00490	— .00508	— .00447	— .00278
90.00	— .00412	— .00622	— .00648	— .00594	— .00398

TABLE III.

## RELATIVE CHANGE OF RESISTANCE.

BISMUTH-TIN ALLOY.  
.53 A% Tin—0°C.

<i>Pressure</i> kg/cm <sup>2</sup>	$\frac{\Delta R}{R_0}$
	<i>Increasing Pressure</i>
2000	.006910
4000	.010168
6000	.008453
8000	.005118
10000	— .001343
12000	— .011940
12446	— .01164
	<i>Decreasing Pressure</i>
12000	— .011352
11000	— .004764
9000	.005947
7000	.014367
5000	.019681
3000	.020707
1000	.013600

## DEDUCTIONS FROM EXPERIMENT.

To illustrate the character of the results, the average pressure coefficient of electrical resistance from 0 to 12000 kg/cm<sup>2</sup> at 30°C and the average temperature coefficient of resistance between the two temperatures are plotted against the per cent composition of the alloy in figures 1 to 3. The curves of pressure coefficients at the other temperature are similar in all respects. The equilibrium diagrams of the alloys have been superposed on these diagrams for



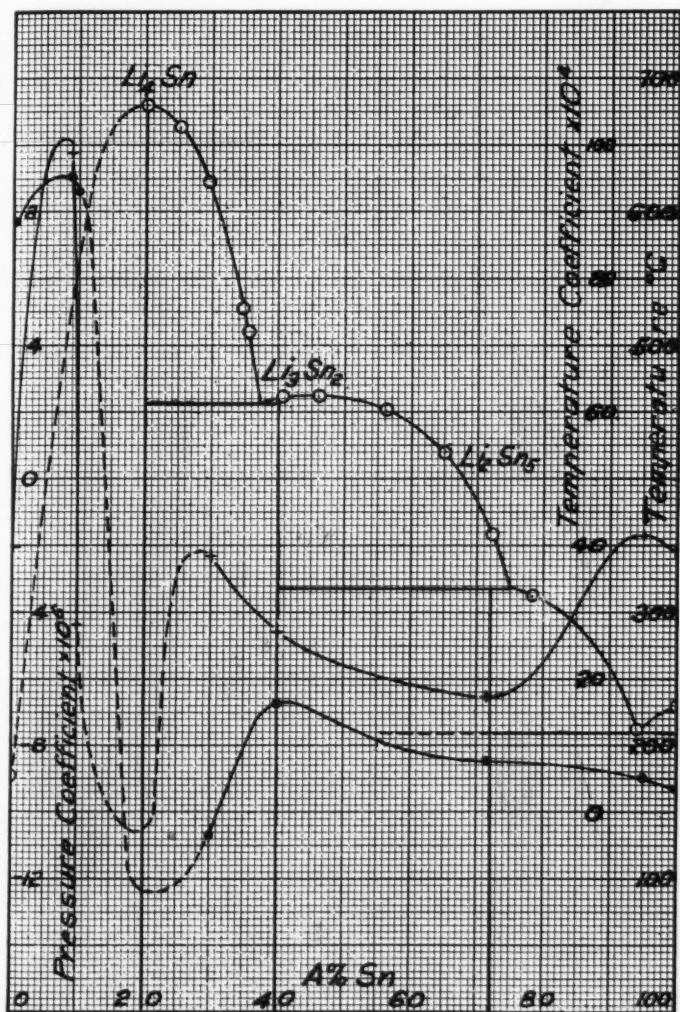


FIGURE 1. Lithium tin series at 30° C. The melting curve is drawn through the circles. The curve through the dots represents the average pressure coefficient of resistance 0–12000 kg/cm<sup>2</sup>. That through the crosses represents the average temperature coefficient of resistance from 30 to 75° C. The abscissae of all three curves are concentrations in atomic per cent tin.

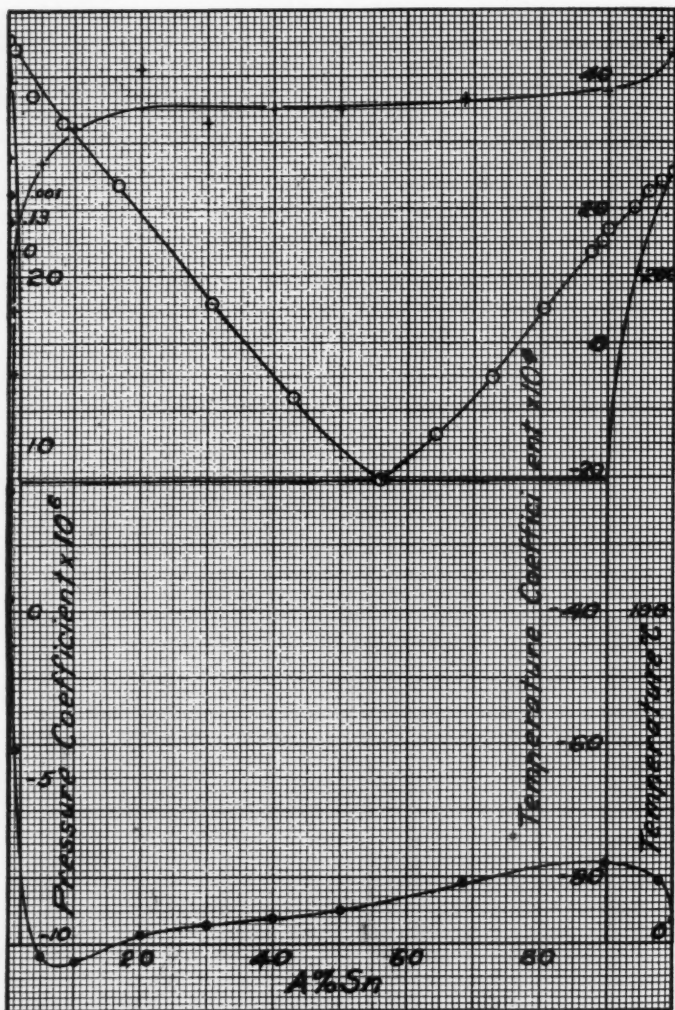


FIGURE 2. Bismuth tin series at  $30^{\circ}\text{C}$ . The melting curve is drawn through the circles. The curve through the dots represents the average pressure coefficient of resistance 0-12000  $\text{kg}/\text{cm}^2$ . That through the crosses represents the average temperature coefficient of resistance from 30 to  $75^{\circ}\text{C}$ . The abscissae of all three curves are concentrations in atomic per cent tin.

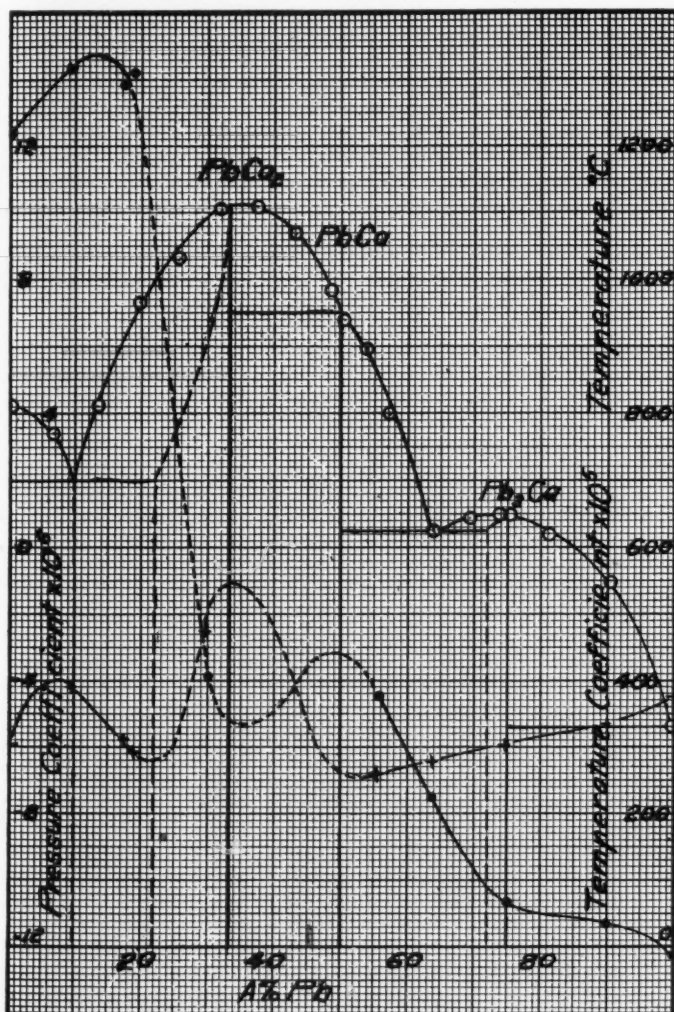


FIGURE 3. Calcium lead series at 30° C. The melting curve is drawn through the circles. The curves through the dots represents the average pressure coefficient of resistance 0–12000 kg/cm<sup>2</sup>. That through the crosses represents the average temperature coefficient of resistance from 30 to 75° C. The abscissae of all three curves are concentrations in atomic per cent tin.

comparison. The equilibrium diagrams for the lithium-tin series have been investigated by Masing and Tammann,<sup>7</sup> the bismuth-tin series by Lepkowski,<sup>8</sup> Bucher,<sup>9</sup> Stoffel,<sup>10</sup> Kapp,<sup>11</sup> Matuyama,<sup>12</sup> and Endo,<sup>13</sup> and the calcium-lead series by Baar,<sup>14</sup> and Donski.<sup>15</sup>

The equilibrium diagrams of the lithium-tin and calcium-lead alloys were taken directly from Masing and Tammann<sup>7</sup> and Donski.<sup>15</sup> There is some confusion in the literature on the equilibrium diagram of the bismuth-tin series because of the three kinds of percent: atomic, weight, and volume. The consensus of opinion seems to be that the eutectic point occurs at 58 W% bismuth or 44 A% bismuth. Bucher's<sup>9</sup> statement that the eutectic point occurs at 58 W% bismuth, or 70.09 A% bismuth, is apparently reversed, since 70.9 W% bismuth is 58 A% bismuth. Stoffel,<sup>10</sup> whom he corrects, was not in need of correction. Again, the International Critical Tables, Vol. 2, p. 416, give an equilibrium diagram, with reference to Kapp,<sup>11</sup> which shows an eutectic point at 58 W% tin. This is apparently in error since Kapp gives 56 W% bismuth as the eutectic mixture. Matuyama<sup>12</sup> gives an equilibrium diagram for bismuth-tin alloys with the eutectic point at about 30 W% bismuth instead of 58 W% bismuth. Comparison of the melting curves found by Lepkowski,<sup>8</sup> Kapp,<sup>11</sup> and Endo<sup>13</sup> shows that Endo's results are a fair average of the other two, so that they were used here. The mean deviation of all the points including Endo's from a smooth curve through his points is 1.7 degrees.

The variations of several physical properties with composition of the alloys have been used to fix the limits of solubility of tin in bismuth and bismuth in tin. The properties so used are the duration time of eutectic crystallization, the electrical conductivity, the temperature coefficient of electrical resistance, the magnetic susceptibility, the thermo-electromotive force, the specific volume, and crystal structure as observed microscopically. These different methods fix the limit of solubility of tin in bismuth between 97.3 and 99.1 A% bismuth and of bismuth in tin between 5.4 and 14 A% bismuth. Endo's<sup>13</sup> values of 98.5 and 9.8 A% bismuth are a fair average. He used all the properties except the thermo-electromotive force.

The curves show a similarity between the lithium-tin and calcium-lead series, as contrasted with the bismuth-tin. The bends in the curves in the lithium-tin and calcium-lead series are apparently caused by the chemical compounds formed by these metals, although the course of the curves is doubtful in the region of the alloys rich in lithium and calcium. There has been some doubt as to whether

calcium belonged to the lithium type or the bismuth type, so that the similarity of these curves for the lithium-tin and calcium-lead series offers evidence that calcium belongs to the lithium type. From figures 1 and 2 it seems plausible that lithium and bismuth should have different types of mechanism to account for their positive pressure coefficients, because of the sudden drop in the coefficient of bismuth with small concentrations of tin; and that the coefficient in bismuth should depend entirely on the crystalline structure of the metal and become normal in the liquid. The positive pressure coefficient in lithium is more stable in its alloys with tin which agrees with the fact that lithium retains its positive coefficient when melted.

Bismuth and tin do not form chemical compounds or mixed crystals, but are soluble in each other up to certain limits between which there is a mechanical mixture of crystals. The bends in the curve of Fig. 2 coincide well with the values of these limits, which, as seen above, have been placed at 9.8 and 98.5 A% bismuth by Endo's measurements. The pressure coefficients of the bismuth-tin alloys in the region of mechanical mixture obey the additive law of mixtures, as expected, so that expressing the concentration in weight per cent, the pressure coefficients in this region from 11 to 70 W% tin may be calculated from the value at the end points.

The physical properties of dilute electrolytes are often similar to those of the pure solvent which has been subjected to pressure. This is approximately true also of the conductivity of a solid solution of bismuth in tin. There is an increase of 1.7% in the volume occupied by one atom of tin in the lattice due to putting 3.6 A% bismuth in tin. The conductivity decreases 7.6% as compared to an increase of 7.8% due to 9200 kg/cm<sup>2</sup>, the pressure required to reduce the volume of pure tin 1.7%. The average pressure coefficient of tin is reduced 17.2% due to putting 3.6 A% bismuth in tin, and 19.7% due to 9200 kg/cm<sup>2</sup>. The corresponding changes in pure bismuth do not agree. 1 A% tin and 3500 kg/cm<sup>2</sup> both decrease the volume of bismuth .9%. 1 A% tin decreases the conductivity 35%, whereas 3500 kg/cm<sup>2</sup> decreases the conductivity 8%. 1 A% tin decreases the pressure coefficient 133%, whereas 3500 kg/cm<sup>2</sup> increases the pressure coefficient 9%. The discrepancy would probably be less if a smaller amount of tin were put into the bismuth lattice, but there is no data for the specific volumes of bismuth tin alloys with less than 1 A% tin.

The curvature of the lithium-tin alloys with the exception of 9

A% tin is greater than that of pure lithium, being about four times as great for the alloy of 30 A% tin, which has the maximum curvature. The curvature is a little less at 75° than at 30°C. The curvature of the calcium-lead alloys is without exception less than that of either calcium or lead, having a minimum of about one-third that of calcium at 29.6 A% lead. The curvature changes little with temperature, being less at 75° than at 30°C for the alloys with 9.5, 17.5, 63.8 and 74.8 A% lead.

The curvature of the bismuth-tin alloys with .13, .53, and .89 A% tin at 0 and 30°C and 5.02 A% tin at 30°C is abnormal, being concave toward the pressure axis. No example of this abnormal curvature has been observed before. Pure bismuth has normal curvature which changes to abnormal when a small amount of tin is added, being largest for the alloy with a .53 A% tin, which has a maximum in the curve of relative change of resistance against pressure. The abnormal curvature decreases again after this maximum is passed, becoming normal at about 5 A% tin, then increasing in magnitude until it passes through a maximum near the eutectic concentration, and finally through a minimum at the solubility limit of bismuth in tin. Heating the crystal slows up these progressive changes of curvature so that they occur at greater tin content at 30 than at 0°C. For example, the curvature has changed to normal in the alloy with 5.02 A% tin at 0, but not at 30°C.

The average temperature coefficients of electrical resistance from 30 to 75°C for the alloys of the lithium-tin and calcium-lead series in Table I are plotted against the concentration in figures 1 and 3. As in the case of the pressure coefficients, the bends in the curves may be correlated with the concentrations at which eutectic points and chemical compounds occur, except for alloys rich in lithium and calcium, where the curves are doubtful. The average temperature coefficients from 0 to 30°C for the alloys of the bismuth-tin series in Table I are plotted against the concentration in figure 2. Again as in the case of the pressure coefficients, bends occur in the curve at the limits of solubility, the curve being nearly straight in the region of mechanical mixtures from 20 to 80 A% tin. The curve does not have a maximum at 71 A% bismuth, as does the curve found by Bucher.<sup>9</sup> He attributed this maximum to the effect of the eutectic point, which he erroneously calculated to exist there. The temperature coefficient becomes negative for solid solutions of tin in bismuth.

The bismuth-tin alloys obey Matthiessen's<sup>16</sup> rule in the region of



mechanical mixtures where the temperature coefficients of the alloys are less by approximately a constant amount than those of the pure metals. This rule does not hold for the lithium-tin nor for the calcium-lead series; nor would this be expected, because of the chemical compounds.

A more accurate account of the variation of the properties of the alloys with temperature is given by the change of the pressure coefficient of electrical resistance with temperature, since this could be more accurately calculated than the temperature coefficient. This is the same as the change of the temperature coefficient with pressure. The relative change of the pressure coefficient of the lithium-tin series with temperature has maxima at 20 and 66 A% tin, and a minimum at 35 A% tin, coinciding roughly with the composition of the chemical compounds  $\text{Li}_4\text{Sn}$ ,  $\text{Li}_2\text{Sn}_5$ , and  $\text{Li}_3\text{Sn}_2$ . The magnitudes of the maxima at 20 A% tin and the minima at 35 A% tin are large compared to the small relative change over the rest of the range of composition. The relative change of the pressure coefficient of the bismuth-tin series with temperature is very small, except in the region of solid solutions of tin in bismuth where there is a sharp peak at .5 A% tin. The relative change of the pressure coefficient of the calcium-lead series with temperature has maxima at 15 and 70 A% lead, which might be correlated with the eutectic point at 11 A% lead and with  $\text{Pb}_3\text{Ca}$ . The curve bends sharply at 22.5 A% lead, where the eutectic mixture of 11 A% lead disappears from the mechanical mixture, and passes through a minimum at 50 A% lead corresponding to  $\text{Pb Ca}$ .

In general, therefore, the relative change of the electrical resistance of the alloys of the three series of lithium-tin, bismuth-tin and calcium-lead with both temperature and pressure may be correlated with the changes in structure of the alloys as given by the equilibrium diagrams.

The change of the solubility limits with pressure in the bismuth-tin series may be determined by comparing the initial and final curves for the instantaneous pressure coefficients at 0 and 12000 kg/cm<sup>2</sup> as a function of concentration. These curves shift .35 A% toward pure bismuth as the pressure increases to 12000 kg/cm<sup>2</sup>, showing that tin becomes less soluble in bismuth as the pressure increases. The curves shift 8 A% away from pure tin toward bismuth as the pressure increases to 12000 kg/cm<sup>2</sup> at the solubility limit of bismuth in tin, showing that bismuth becomes more soluble in tin as the pressure increases.

From each curve of figures 1, 2, and 3, it may be seen that putting a foreign metal into a pure one increases the pressure coefficient of resistance of the pure metal algebraically. Since these curves for all pure metals have a normal curvature, hydrostatic pressure also increases the pressure coefficient. If this held in general, it would be justifiable to conclude that putting foreign atoms into the crystal lattice of any metal increases the algebraic value of the pressure coefficient of resistance, regardless of whether the pressure coefficient is positive or negative or what foreign metal is used. Further, hydrostatic pressure on the lattice has precisely the same effect. This is true not only of the metals in these experiments, but also of the alloys of iron with nickel and cobalt, measured by Bridgman but not yet published.

This relation also holds for the copper-manganese series measured by Lisell,<sup>2</sup> where a small amount of manganese increased the value of the pressure coefficient of copper from a negative to a positive one. The gold-silver, cadmium-lead, and gold-nickel series, whose pressure coefficients have been measured by Beckman<sup>3</sup>, also follow this rule. The case of cadmium-lead alloys rich in cadmium is apparently an exception, but if Beckman's  $\alpha = 103 \times 10^{-7}$  is replaced by  $115 \times 10^{-7}$  as calculated from Bridgman's data for pure cadmium,<sup>12</sup> there will be a minimum in Beckman's curve and no exception. The points on the curve near pure cadmium show a tendency to rise, suggesting that Beckman's value for pure cadmium is too low. Beckman has plotted negative coefficients as though they were positive.

Platinum iridium and German silver were also found by Lisell<sup>2</sup> to have pressure coefficients which are greater than the coefficients of either of the pure metals of which they are composed, so that the pressure coefficient concentration curves have a maximum, indicating that the pressure coefficients of the pure metals are probably increased by impurities.

Putting foreign atoms into the crystal lattice of a pure metal, especially in a solid solution, as in the bismuth-tin series, causes the lattice to expand or contract as a whole. Similarly hydrostatic pressure causes the lattice to contract. Since the pressure coefficients of electrical resistance are similarly altered by these two processes, it seems probable that the conductivity of a metal depends on the arrangement of its atoms in space, or on the geometrical configuration of the crystal lattice. These experiments do not give a basis for explaining the positive pressure coefficients of lithium, calcium, and bismuth by an atomic mechanism, as it was hoped they would do.



## SUMMARY.

The pressure coefficients of electrical resistance for the alloys of the three series lithium-tin, bismuth-tin, and calcium-lead for different concentrations, collected in Table I, constitute the principal experimental results.

These experiments show that distorting the crystal lattice by inserting foreign metals has the same effect on the pressure coefficient as does distorting the lattice by hydrostatic pressure. The change in the pressure coefficient is independent of the metal inserted in the crystal lattice.

Finally, it seems probable from these considerations that the mechanism of electric conduction in metals is connected with their geometrical configuration, the phenomena depending on the type of the crystal lattice and its uniformity or distortion.

I take pleasure in thanking Professor Bridgman for his interest and assistance. In particular, I appreciate his ideas which, suggested at the difficult points, have made this research possible.

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## REFERENCES.

- <sup>1</sup> P. W. Bridgman, (a) Proc. Am. Acad. 52, 573, 1917.  
(b) Proc. Am. Acad. 56, 61, 1921.  
(c) Proc. Am. Acad. 58, 151, 1923.  
(d) Proc. Am. Acad. 59, 109, 1923.  
(e) Proc. Am. Acad. 62, 207, 1927.
- <sup>2</sup> E. Lisell, Om Tryckets Inflytande på det Elektriska Ledningsnotstandet hos Metaller samt en Ny Metod att Mäta Höga Tryk, Uppsala, 1902.
- <sup>3</sup> B. Beckman, (a) Uppsala Universitets Arsskrift 1911, Matematik och Naturvetenskap, 1.  
(b) Arkiv För Matematik, Astronomi, och Fysik 7, No. 42, 1912.
- <sup>4</sup> P. W. Bridgman, Proc. Am. Acad. 47, 335, 1911.
- <sup>5</sup> A. Bucher, ZS. anorg. Chem. 98, 118, 1916.
- <sup>6</sup> P. W. Bridgman, Proc. Am. Acad. 57, 101, 1922.
- <sup>7</sup> G. Masing and G. Tammann, ZS. anorg. Chem. 67, 193, 1910.
- <sup>8</sup> W. v. Lepkowski, ZS. anorg. Chem. 59, 287, 1908.
- <sup>9</sup> A. Bucher, ZS. anorg. Chem. 98, 117, 1916.
- <sup>10</sup> A. Stoffel, ZS. anorg. Chem. 53, 148, 1907.

- <sup>11</sup> A. W. Kapp, Diss. Königsberg, 1901.  
Annalen der Physik 6, 754, 1901.
- <sup>12</sup> Y. Matuyama, Sci. Rep. Tohoku Imp. Univ. 16, No. 4, 464, 1927.
- <sup>13</sup> H. Endo, Sci. Rep. Tohoku Imp. Univ. 14, 489, 1925.
- <sup>14</sup> N. Baar, ZS. anorg. Chem. 70, 375, 1911.
- <sup>15</sup> L. Donski, ZS. anorg. Chem. 57, 210, 1908.
- <sup>16</sup> A. Matthiessen, Pogg. Anallen 122, 47, 1864.

